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A hybrid Pt/NbO/CNTs catalyst with high activity and durability for oxygen reduction reaction in PEMFC

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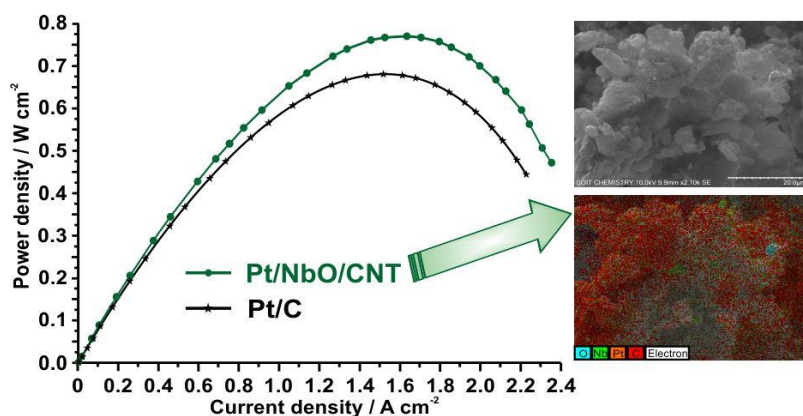
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Graphical Abstract



Highlights

- NbO suboxide support catalyst was prepared from Nb₂O₅.
- Pt/NbO/CNTs catalysts prepared from NbO suboxide and multi-wall carbon nanotubes.
- Excellent ORR activity & high durability after load cycling and startup/shut down stability test.
- Excellent activity in PEMFC with 772 mW cm⁻² (Pt loading @ cathode: 0.15 mg cm⁻²).
- Outstanding MEA stability with only 4% power loss.

30 *Abstract*

31 To improve the kinetics and durability of Pt-based electrodes toward the oxygen reduction reaction (ORR), high
32 electroactive and stable catalysts were synthesized by depositing Pt over niobium oxide (NbO) supported on
33 commercial multi-wall carbon nanotubes (CNTs). The Pt/NbO/CNTs, exhibits excellent electroactivity and stability
34 toward ORR, reaching a high electroactivity of $57 \text{ mA mg}_{\text{Pt}}^{-1}$, higher than the Pt/CNTs and commercial Pt/C (20%
35 Pt/C HiSPECTM). Moreover, the developed Pt/NbO/CNTs demonstrated outstanding durability under accelerated
36 stress testing (AST) according to load cycling and startup/shutdown stability protocols. Proton exchange membrane
37 fuel cells (PEMFC) tests with an MEA fabricated using Pt/NbO/CNTs showed excellent performance, with a low
38 Pt loading down to 0.15 mg cm^{-2} , achieving a maximum power density of 772 mW cm^{-2} . Furthermore, a short-term
39 durability test in PEMFC demonstrated only a 4% loss on the maximum power density at $80 \text{ }^{\circ}\text{C}$. The superior
40 electrocatalytic activity and durability of Pt/NbO/CNTs can be ascribed to the anchoring effect of Pt nanoparticles
41 over the NbO/CNTs hybrid support, showing that the developed Pt/NbO/CNTs is a promising durable electrocatalyst
42 for PEMFC applications.

43

44 **Keywords:** Proton exchange membrane fuel cells (PEMFC); Metal oxide support; Platinum electrocatalyst; Oxygen
45 reduction reaction (ORR); Corrosion-resistance support; Stability and durability.

46

47 **1. Introduction**

48 Proton exchange membrane fuel cells (PEMFC) have attracted the consideration of many researchers as a highly
49 efficient and clean energy source. Since one of principal drawback of electrocatalysts for oxygen reduction reaction
50 (ORR) is their slow kinetics reaction, extensive studies on highly active and durable electrocatalysts have been
51 performed, focusing to improve both ORR kinetics and durability [1-12]. Pt supported on carbon-based materials is
52 one of the most common electrocatalysts for PEMFCs cathodic ORR [13]. However, the degradation of carbon
53 supports and high Pt loading significantly hinder the wide adoption of PEMFC. The carbon corrosion, and the
54 consequent loss of Pt nanoparticles (NPs), causes drastic reduction in electroactivity. This effect is particularly
55 evident under harsh operating conditions of PEMFC, especially during prolonged open-circuit potential (OCP) or
56 under repeated start up/shout down cycles [1,2,5,6]. To mitigate these problems, the use of metal oxides has been
57 considered as an alternative method to promote an increased electroactivity and stability of Pt electrocatalyst. Metal
58 oxides such as TiO_2 , NbO_2 , RuO_2 , MoOx , exhibit high catalytic activity and strong interaction band with Pt [3,4,7–
59 12,14]. Metal oxide supports provide a strong interfacial active band and enhance the catalytic activity towards
60 ORR. Such an effect is attributed to the behavior of Pt electronic structure, which causes a decline in OH adsorption
61 on Pt surface, through lateral repulsion from the OH or O on the oxide's surface [1]. This approach leads to
62 decreasing the amount of noble metals required in the electrocatalyst, while increasing the electrocatalytic activity
63 and durability. Moreover, by employing oxide metals as support materials, a more stable and homogeneous
64 dispersion of Pt NP can be achieved [15–21].

65 NbO is a well-known reducible metal oxide, which shows high oxygen storage capacity with strong metallic
66 interaction with Pt NP, displaying high conductivity, excellent catalytic stability, and corrosion resistance [1,12,22–
67 28]. This study demonstrates the use of NbO, mixed with carbon nanotubes (CNTs), can promote electrocatalytic

68 activity and durability of Pt electrocatalyst. In fact, Pt/NbO/CNTs electrocatalysts exhibit higher electrocatalytic
69 activity and stability compared to commercial Pt/C (HiSPEC™ 3000) electrocatalyst. Developing highly active and
70 stable low Pt-based electrocatalyst for ORR will be the key action to enhancing PEMFC efficiency to deliver
71 reliable, affordable, and environmental friendly energy.

72

73 **2. Experimental**

74 **2.1 Chemicals**

75 Commercial multiwall carbon nanotubes (CNTs: 6-9 nm × 5 μm 95 wt.%), chloroplatinic acid hexahydrate
76 (H₂PtCl₆·6H₂O, ≥37.50% Pt basis), sodium borohydride (NaBH₄, 98 wt.%), potassium hydroxide (KOH, 85%
77 purity), sodium hydroxide (NaOH, 85% purity), ethylene glycol (EG, 98 wt.%), polyvinylpyrrolidone (PVP, 98
78 wt.%), sulphuric acid 95-98 wt% (H₂SO₄), nitric acid (HNO₃, 70 wt.%), chloridric acid (HCl, 37 wt.%), Nafion®
79 perfluorinated resin solution (5 wt.%), acetone (C₃H₆O, 99.5 wt.%), ethanol (C₂H₆O, 99.8 wt.%), 2-propanol (C₃H₈O,
80 99.5 wt.%), and Nafion® membrane NRE212 were purchased from Sigma-Aldrich. Niobic acid (Nb₂O₅·nH₂O, type
81 HY-340, water content ≈20 wt.%) was supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM,
82 Brazil). A commercial 20 wt.% Pt/C (HiSPEC™ 3000, Johnson Matthey) was used for comparison test. All aqueous
83 solutions were prepared using ultrapure deionized water (DW) obtained from a Millipore Milli-Q system with
84 resistivity >18 mΩ cm⁻¹. Ultrapure N₂, O₂, and H₂ gasses were purchased by SIAD.

85

86 **2.2 Synthesis of NbO**

87 5 g Nb₂O₅·nH₂O was dispersed in 70 mL of 5 M NaOH aqueous solution under stirring for 2 h. Then, the prepared
88 solution was transferred into a Teflon autoclave for a hydrothermal treatment at 120 °C for 50 h to obtain NbO_x.
89 Subsequently, the treated NbO_x was washed with DW and 0.1 M HCl aqueous solution until the pH reached to
90 values lower than 7. After that, the obtained NbO_x was filtered and dried in air at 100 °C for 2 h. The synthesized
91 NbO_x was annealed at 950 °C (heating rate of 5 °C min⁻¹) for 4 h under a reducing atmosphere (H₂:N₂ 10:90 vol.%)
92 to obtain NbO.

93

94 **2.3 Synthesis of hybrid support NbO/CNTs**

95 100 mg CNTs was added to a solution of EG and ethanol (40:10 ml) and left stirring for 20 min. 1 wt.% PVP was
96 added to the solution and left stirring for 2 h. The previously synthesized NbO was initially dispersed in EG, then
97 added to the solution containing the CNTs and left stirring for 3 h. Then, the pH was reduced to 5 by adding HNO₃,
98 and left stirring for 5 h. The obtained solution was filtered and washed with ultra-pure DW and left dry at 100 °C.
99 The CNTs supported NbO (NbO/CNTs) was then annealed at 500 °C (heating rate of 10 °C min⁻¹) for 4 h under a
100 reducing atmosphere H₂:N₂ 10:90 vol.%.

101

102 **2.4 Synthesis of Pt/NbO/CNTs**

103 Pt/NbO/CNTs electrocatalysts were synthesized via the modified polyol method. NbO/CNTs was added to solutions
104 of EG and ethanol (40:10 ml) and left stirring for 1 hr. Then, 1 wt.% PVP was added to the solution. 53 mg of

105 $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ (corresponding to 0.04 mmol of Pt) was dissolved into EG, added to each solution containing the
106 NbO/CNTs and left stirring for 3 h at pH 11. The solution was heated to 120 °C under water-cooled reflux condenser
107 for 5 hr. Then, temperature was reduced to 20 °C and solution was kept stirring for 5 h. The pH of the solution was
108 brought to 4 by adding HNO_3 and left stirring for 12 h. The obtained solution was filtered, washed with DW, and
109 the collected samples were dried at 100 °C. The obtained Pt/NbO/CNTs catalysts were annealed at 400 °C (heating
110 rate of 5 °C min^{-1}) for 4 h under a reducing atmosphere ($\text{H}_2:\text{N}_2$ 10:90 vol.%). For sake of comparison, a Pt/CNTs
111 with same Pt amount was prepared.

112

113 **2.5 Chemical-physical characterization of the electrocatalysts**

114 The morphology of the synthesized electrocatalysts and the quantification of the metals content were observed by
115 using a scanning electron microscopy (SEM) coupled with an energy dispersive X-ray (EDX) detector (Hitachi
116 FlexSEM 1000). Transmission electron microscopy (TEM) was carried out using a Philips CM12 microscope.
117 Thermogravimetric analysis (TGA) was performed using a TA Instruments Q600 SDT thermal analyzer. The
118 Sample was heated from room temperature to 1000 °C at a rate of 10 °C min^{-1} under flowing air (20 mL min^{-1}),
119 which enables the determination of the weight percent of the individual components. The phases and lattice
120 parameters of the composite catalyst was characterized by using X-ray diffraction (XRD) employing Panalytical
121 X'Pert PRO diffractometer with a PIXcel detector. The Cu $K\alpha$ radiation, ($\lambda = 0.15418 \text{ nm}$) operating at 40 kV and
122 30 mA used under the conditions of $2\theta = 10\text{--}100^\circ$ and 2θ step size = 0.03. The average crystallite size of the Pt
123 particles was estimated using the Scherrer equation. The specific surface area of samples was determined by the
124 Brunauer-Emmet-Teller (BET) method using a Quantachrome Nova 1200e BET analyzer within the relative
125 pressure range of 0.1-0.9. Nitrogen adsorption isotherms were recorded at -196 °C within the relative pressure range
126 of 0-1. Prior to adsorption, samples were placed in the cell and evacuated at 150 °C for 3 h under high vacuum. The
127 surface composition of the NbO/CNTs and Pt/NbO/CNTs support and catalyst were studied by XPS, employing the
128 Thermo Scientific K-Alpha Angle-Resolved system equipped with a monochromatic Al $K\alpha$ (1486.7 eV) X-ray
129 source and a 180° double focusing hemispherical analyzer with a 128-channel detector with effective charge
130 compensation.

131

132 **2.6 Electrochemical characterization of the electrocatalysts**

133 The electrochemical evaluation of the Pt/NbO/CNTs, Pt/CNTs and Pt/C electrocatalysts were carried out in a three-
134 compartment electrochemical cell using a multi-potentiostat (Bio-Logic SP150) and a rotating disk electrode
135 instrument (RRDE-3A ALS Model 2323) or Pine Instruments. The electrochemical cell was equipped with a glassy
136 carbon (GC) or gold disk working electrode (0.1256 cm^2), a graphite rod as a counter electrode, and a saturated
137 calomel (SCE) as a reference electrode (each experiment repeated for three times). All potentials reported here were
138 corrected to the RHE scale. The procedure for preparing the electrocatalyst ink and the RDE is reported in our
139 previous study [29]. The Pt loading on the GC/gold electrode was 20 $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$, corresponding to 3 μL of the
140 sonicated ink, micropipetted from the ink, deposited over working electrode and dried at room temperature. The
141 Nafion[®] ionomer-to-catalyst ratio in the ink was equal to 0.1.

142 Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed in N₂-
143 saturated 0.5 M H₂SO₄ or 0.1M H₂SO₄ aqueous solution. CV were recorded varying the voltage in the range 0.05 to
144 1.25 V_{RHE}. Impedance spectra were collected over a frequency range of 100 kHz to 0.1 Hz at a DC bias potential of
145 0.425 V_{RHE} using Solartron 1470 multichannel potentiostat paired with a Solartron 1260 frequency response
146 analyzer, controlled using Multistat software (Scribner Associates). ORR activity was assessed using linear sweep
147 voltammetry (LSV) at rotating disk electrode in O₂-saturated 0.5 M H₂SO₄ aqueous solution. The electrochemical
148 surface active area (ECSA, m² g⁻¹) of the various electrocatalysts was determined from the Pt hydrogen desorption
149 region between 0.06 V and 0.36 V_{RHE}, by integrating the total charge, normalizing with scan rate, Pt loading, and
150 assuming a surface charge density of 210 μC cm⁻² for a monolayer adsorption of hydrogen on Pt surface [2,30,31],
151 according to the following formula:

$$152 \quad ECSA = \frac{Q_H}{0.21 \cdot [Pt]}$$

153 CO stripping voltammetry (CO-SV) was performed in 0.5 M H₂SO₄ at a scan rate of 20 mV s⁻¹ in the potential range
154 of 0.05-1.25 V_{RHE}. Before the analysis, a flow-rate of CO was pre-adsorbed for 20 min while maintaining the
155 working electrode at the constant potential of 0.06 V_{RHE}. Then, a flow rate of pure N₂ was introduced for 20 min to
156 remove the excess CO dissolved in the solution before stripping the CO. The ex-situ electrochemical stability of the
157 supports and catalysts were evaluated using ASTs that involved repeated cycling of the working electrode based on
158 triangular-wave form at different potential range according to protocols developed by US Department of Energy.
159 This potential ranges assures the accelerated corrosion of the support as well as the sintering of Pt NPs based on Pt
160 oxide growth/removal, load cycling and start up/shut down fuel cells condition. The electrode health was monitored
161 by periodic CV and EIS assessment throughout the AST. In addition, the ORR activity of each electrocatalysts was
162 assessed before and after the AST.

163

164 2.7 PEMFC tests

165 The Pt/NbO/CNTs was used for a series of electrochemical tests in a Electrochem PEMFC station, and compared
166 with Pt/C commercial. Nafion® 212 membranes were cleaned and fully protonated before use by first immersing
167 them in 3% H₂O₂ at 80 °C for 1 h, then in 0.5 M H₂SO₄ at 80 °C for 2 h, and finally washing them in ultrapure DW
168 for 2 h changing water every 30 min. The catalyst inks were prepared through dispersion of the electrocatalyst in a
169 mixture of isopropanol and DW, and 32 wt.% Nafion® ionomer, and sonicating in ultrasonic bath for 30 min. The
170 Pt loading was set at 0.15 mg_{Pt} cm⁻² for both for Pt/NbO/CNTs and Pt/C electrocatalysts. Both electrodes were
171 prepared through spray deposition onto the gas diffusion electrodes (E-TEK ELAT), and then the electrodes dried
172 at 70 °C. The MEA were assembled by hot-pressing the electrodes on the two sides of each membrane at 20 kg cm⁻²,
173 50 bar, and 120 °C, for 90 sec.

174 PEMFC tests were performed by feeding pure fully humidified compressed hydrogen and oxygen, 120 and 200
175 NmL min⁻¹, respectively, at 1 bar backpressure. Before performing polarization curves, each membrane was
176 conditioned with a series of 10 cycles running the cell at 0.6 V_{RHE} for 30 min and then at 0.4 V_{RHE} for another 30
177 min, and finally opening the circuit for 1 min, at a temperature of 70 °C [32]. Polarization curves were determined

178 at 30, 50, 70, and 80 °C. A durability tests were then performed on fresh MEA, maintaining it in operation at the
179 maximum current density at 80 °C for 96 consecutive hours, repeating polarization curves every 24 h.

180

181 3. Results Discussion

182 3.1 Physical-chemical characterization of support and electrocatalysts

183 **Figure 1** shows the XRD structural characterization of CNTs, Nb₂O₅, NbO, NbO/CNTs hybrid supports, and
184 Pt/(NbO)/CNTs electrocatalysts. The starting CNTs has a large broad peak at $2\theta = 26.1^\circ$, corresponding to graphite
185 {002} reflection plane [33,34]. The starting Nb₂O₅ has typical peak orientations at $2\theta = 26.3^\circ$ {400}, 54.5° {622},
186 which its structure transferred to suboxide NbO after autoclave and heat treatment. The NbO/CNTs hybrid supports
187 show the typical peaks corresponding to NbO, with characteristic reflections at $2\theta = 36.2^\circ$ {111}, 42.2° {200}, 60.9°
188 {220}, 73.1° {311}. The Pt/NbO/CNTs catalysts have peaks orientation at $2\theta = 40.32^\circ$ {111}, 46.75° {200}, 68.1°
189 {220}, 81.8° {311}, and 86.1° {222}, which are indexed to the face-centered cubic structure of Pt crystallites present
190 on NbO/CNTs hybrid supports. Compared to the standard card of Pt (ICDD card 01-087-0640), all corresponding
191 Pt peaks were shifted toward higher angles, indicating a diminution of lattice spacing. This phenomenon can be
192 attributed to the strong metallic support interaction (SMSI) between Pt NPs and NbO/CNTs hybrid support [35].
193 Moreover, the peak at $2\theta = 40.32^\circ$ is broad and intense, sign that Pt NPs are essentially orientated towards the Pt
194 {111} plane, that is the most stable and highly active toward ORR. In fact, this plane contains hexagonally packed
195 Pt atoms and does not undergo surface reconstruction, unlike Pt {100} and Pt {110} surfaces [2,35,36]. The Pt
196 crystallite sizes were calculated from the widths of the {220} peaks using the Scherrer-Debye equation. The mean
197 crystallite size of Pt particles obtained was in the range of 2-4 nm, which is in good agreement with TEM results.

198 **Figure 2** shows the TEM and overall SEM image obtained for Pt/NbO/CNTs catalyst at different magnifications.
199 The Pt NPs are well dispersed over the NbO/CNTs support (**Fig 2a**), where the TEM (HRTEM) image showed Pt
200 NPs were dominated by octahedron {111}-*d*-spacing of ~ 0.223 nm in agreement with XRD result (**Fig. 2b-2c**) [37–
201 39]. **Figure 2c** demonstrate the lattice fringe of NbO nanoparticles. The fringe spacing is calculated to be ~ 0.375
202 nm ± 0.01 nm, corresponding to the {001} lattice spacing. Compare to Nb₂O₅ with *d*-spacing of 0.39 nm ± 0.01 nm,
203 the NbO exhibited reduced *d*-band due to oxygen vacancy in its lattice structure [40–42]. **Figure (2d-2f)** shows
204 overall SEM image of Pt/NbO/CNTs catalyst with the relative EDS elemental distribution map. Figure 2f shows Pt
205 nanoparticles are finely distributed over NbO/CNTs hybrid support with no sign of agglomeration or cluster
206 formation.

207

208

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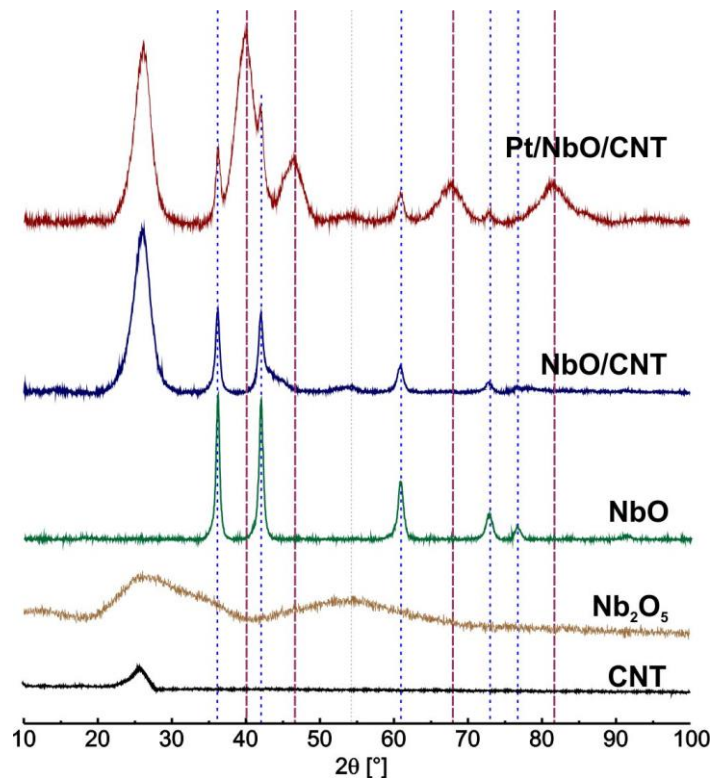


Figure 1. XRD pattern of CNTs, Nb₂O₅, NbO, Nb/CNTs, and Pt/NbO/CNTs electrocatalysts.

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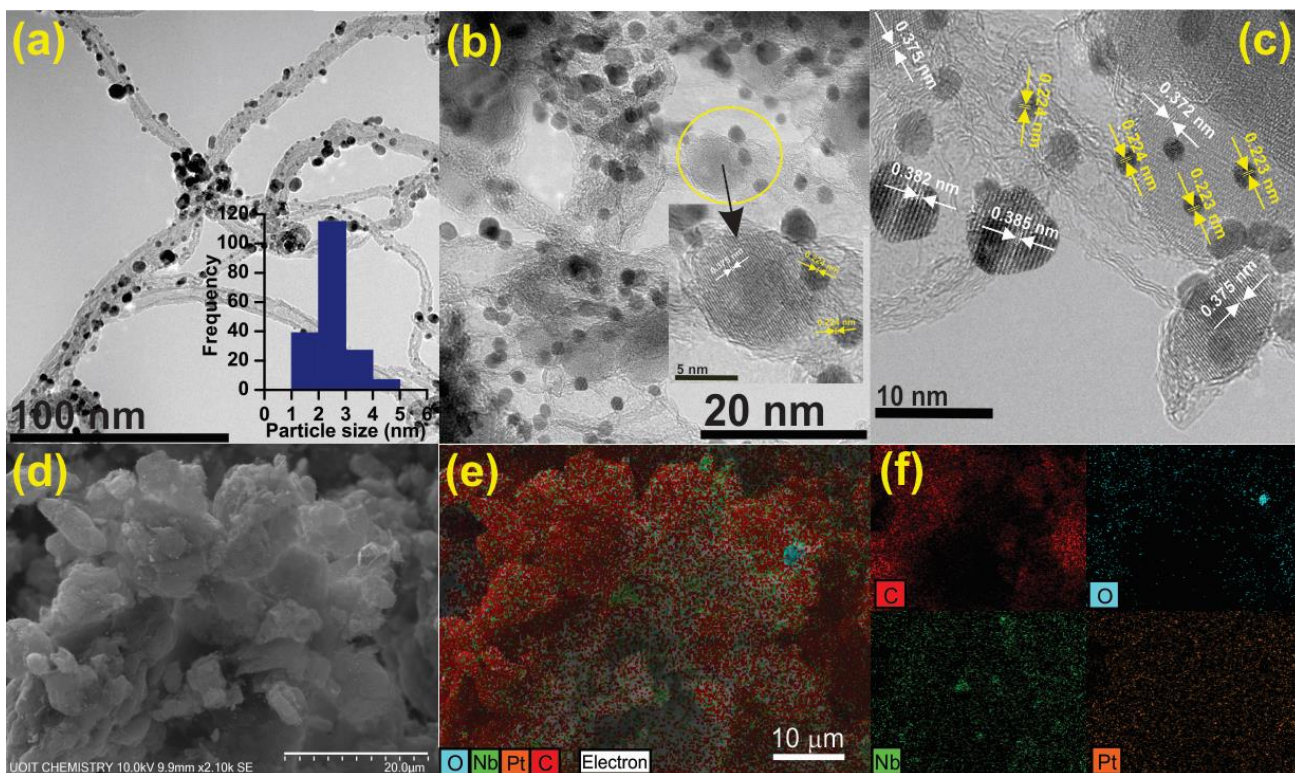


Figure 2. (a, b and c) TEM image corresponding to Pt/NbO/CNTs, (d, e and f) SEM-EDX elemental mapping obtained for Pt/NbO/CNTs electrocatalyst.

211

212 The electronic interaction between Pt and the NbO/CNTs hybrid support were investigated by using XPS spectra
 213 and the results are shown in (**Fig. 3**). The Nb double peaks of 3d_{5/2} and 3d_{3/2} levels with splitting-value of Δ= 2.78
 214 eV were located at binding energies of 207.42 eV and 210.2 eV, respectively [43,44]. Compare to pure Nb₂O₅ with

215 Nb double peaks of $3d_{5/2}$ and $3d_{3/2}$ levels at 207.1 eV and 209.88 eV binding energies, the reduced NbO oxide
 216 exhibited binding energies of 207.42 eV and 210.2 eV. In fact, 0.32 eV shift to higher binding energy in the Nb 3d
 217 levels compared to defect-free Nb_2O_5 is caused by surface oxygen vacancy defects in the NbO support (**Fig. 3a**).
 218 Furthermore, it was found out for Pt/NbO/CNTs, the NbO peaks were shifted to higher binding energy by 0.18 eV
 219 compared to Nb of NbO/CNTs (0.5 eV compared to pure Nb_2O_5) (**Fig. 3b**). Such this shift to higher binding energy
 220 could be due to Pt-NbO metallic binding. The Pt analysis shows doublet peaks in the 4f region referring to $4f_{7/2}$ and
 221 $4f_{5/2}$, where the deconvolution of the Pt spectrum reveals two pairs of separate doublet peaks in each region. The
 222 high intensity doublet peaks with splitting-value of $\Delta = 3.35$ eV attributed to metallic Pt (Pt^0), located at the binding
 223 energies of 71.7 eV and 75.05 eV, respectively [12,45,46]. The peak at binding energy of 71.7 eV, referring to Pt^0
 224 $4f_{7/2}$ reveals 0.7 eV positive shift towards higher binding energy compared to the $4f_{7/2}$ conventional value of Pt/C.
 225 This shift to higher binding energy corresponds to induced positive charge on the dispersed Pt NPs due to the
 226 interaction between Pt NPs and NbO support through SMSI effect which positively influenced the d-band state of
 227 Pt NPs [47–49]. Moreover, the low-intensity doublet peaks at binding energies of 73.42 eV and 76.76 eV assigned
 228 to Pt^{2+} species due to surface oxide/hydroxide (**Fig. 3c**).

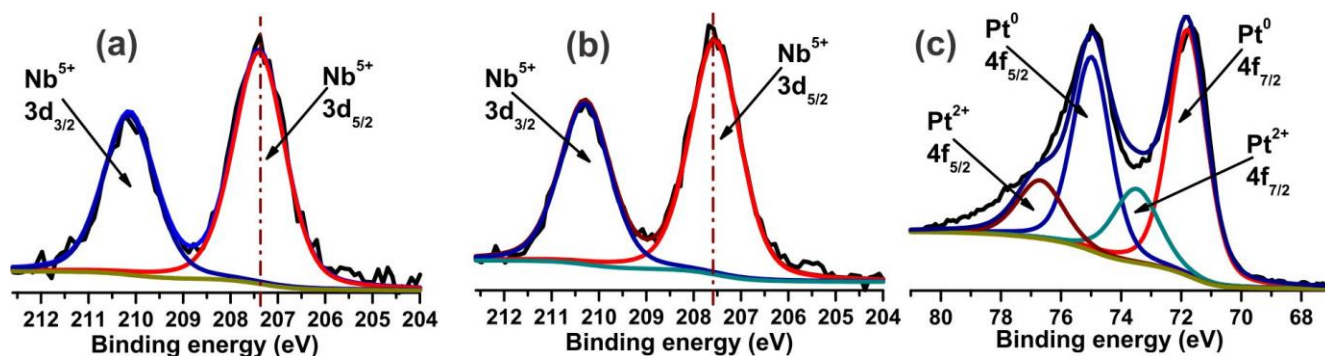


Figure 3. XPS spectra of the (a) NbO/CNTs support, (b) and (c) Pt/NbO/CNTs catalyst.

230

231 **Figure 4** shows the TGA and DTG curves obtained under flowing air for CNTs, NbO/CNTs, and Pt/NbO/CNTs
 232 samples. All samples showed moisture and volatile matter loss in temperature range of 80-250 °C. The CNTs
 233 underwent carbon combustion in two step, the main weight loss occurs in temperature range of 450-600 °C due to
 234 the oxidation of un-filled CNTs [50,51]. The second weight loss of CNTs that occurs at slight higher temperature is
 235 referred to the oxidation of polyaromatic carbon shells present in the CNTs, due to ethanol as a carbon source
 236 [52,53]. The NbO/CNTs exhibited carbon combustion between 500-650 °C due to the presence of NbO, which
 237 shield the CNTs. On other hand, the Pt/NbO/CNTs shows carbon combustion in a lower temperature range, between
 238 420-520 °C, due to presence of Pt catalyst, which facilitates the combustion reaction. The residual weight percentage
 239 of samples at 800 °C was used to calculate the weight percentage of NbO and Pt content. Moreover, the TGA and
 240 DTG analysis of samples under inert atmosphere (Argon) are presented in (**Fig. S1**).

241 The surface areas and porous characteristics of CNTs and NbO/CNTs support were investigated by nitrogen
 242 ad/desorption measurements. The BET isotherms and BJH pore size distribution curves of both support are shown
 243 in (**Fig. 4c**). Both of CNTs and NbO/CNTs supports show typical type IV isotherms indicating the presence of
 244 mesoporous structure. Upon deposition of the NbO, the surface area of CNTs slightly reduced from $364.1 \text{ m}^2 \text{ g}^{-1}$ to

245 331.1 m² g⁻¹ due to NbO particles which physically block access to some of the CNTs pores [54]. The changes in
 246 BET surface area, pore volume and size of CNTs after NbO deposition reported in **Table 1**. The pore size distribution
 247 plots from the nitrogen adsorption isotherm of the CNTs and NbO/CNTs were presented in the inset of (**Fig. 4c**).
 248 Both support presented pore size distribution peak approximately in range of 2 nm to 15 nm with an average diameter
 249 of 4-6 nm, which indicate the CNTs and NbO/CNTs exhibited mesoporous structure with high surface, suitable
 250 support for Pt electrocatalyst.

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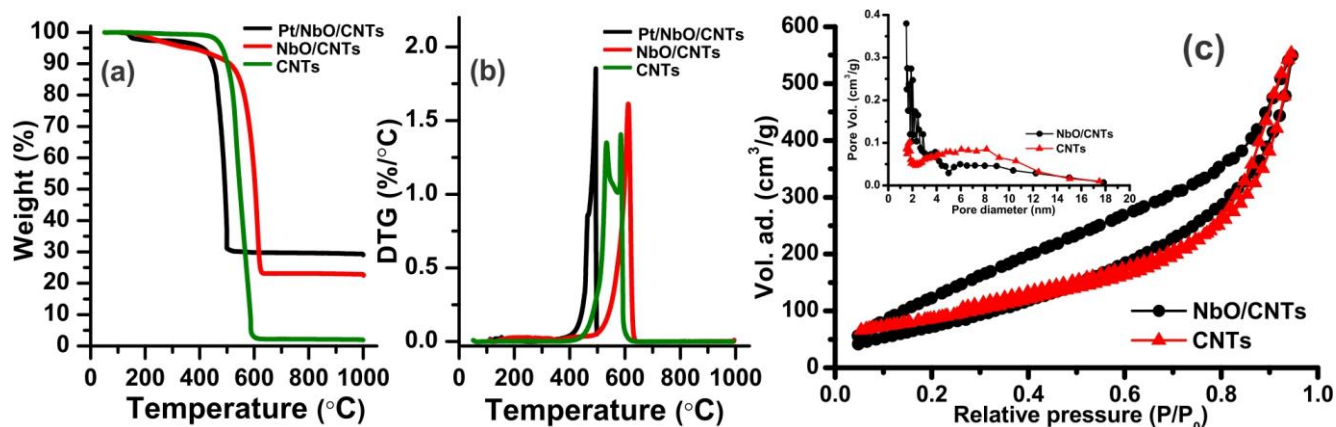


Figure 4. Air-thermo analysis of CNTs, NbO/CNTs, and Pt/NbO/CNTs; (a) TGA, (b) DTG, (c) BET surface area analysis via nitrogen ad/desorption isotherms and corresponding pore size distribution (inset) of CNTs, NbO/CNTs.

252

Table 1. BET analysis of supports

Sample	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Pore size [nm]
NbO/CNTs	331.1	0.754	1.56
CNTs	364.1	0.885	1.98

253

254 3.2 NbO support electroactivity and stability

255 **Figure 5** shows the electrochemical activity of NbO support. The CV of NbO exhibited small reversible redox
 256 peaks, typical for pseudo-capacitive materials. The CV results reveal that NbO does not contribute during hydrogen
 257 ad/desorption regime, and no specific oxidation or reduction current peak observed, a sign of NbO high stability in
 258 acid medium [55]. The AST results on NbO up to 5,000 cycles indicates that NbO is perfectly stable in 0.5 M H₂SO₄
 259 aqueous electrolyte over the entire range of applied potential (**Fig. 5a**). The ORR activity of NbO support was
 260 assessed before the AST (**Fig. 5b**). The NbO exhibits limited activity, with onset potential of 0.7 V_{RHE} for O₂
 261 reduction followed by high half-wave potential of 0.2 V_{RHE}. **Figure 5c-5d** displays the EIS response of the NbO
 262 support over the course of the AST; data is shown as Nyquist and capacitance plots. During a stability test, the key
 263 parameters to monitor is the length of Warburg region in order to determine any changes in R_Σ (R_Σ = R_{electronic} +
 264 R_{ionic}) and C_{dl} (low frequency limiting capacitance) which is indicative of any changes in the interfacial surface area
 265 of the electrode. The Nyquist plot of NbO support exhibited short Warburg regions assign to its high electronic and
 266 ionic conductivity. The Warburg length slightly decreased over the course of the stability test due to enhance
 267 accessibility of catalyst surface layer to electrolyte solution and consequently enhancing the total conductivity of

268 catalyst layer [46,56]. The limiting capacitance of NbO shows visually no change over the course of 5,000 cycles,
 269 assign to highly stable catalyst surface layer (Fig 5e-5f).

270

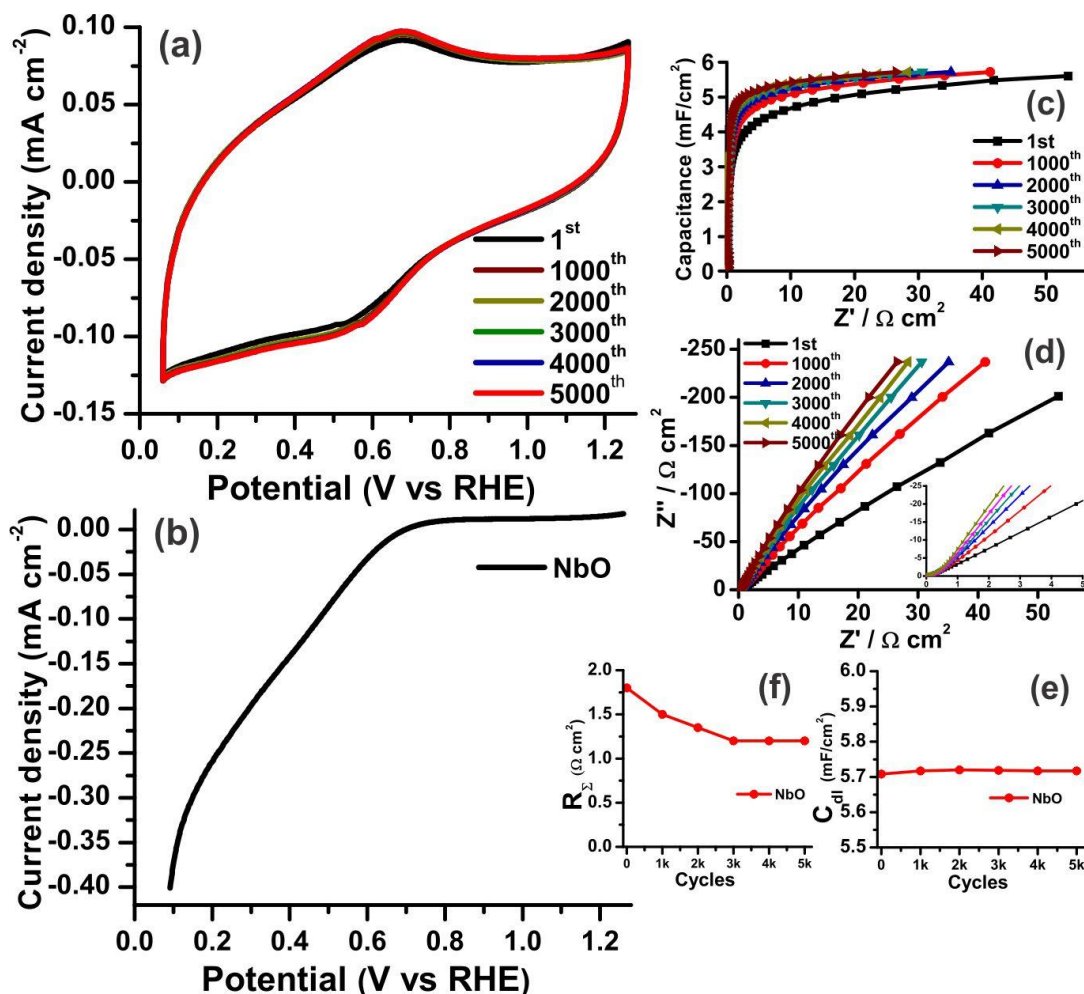


Figure 5. (a) CV recorded in 0.5 M H₂SO₄ N₂-saturated solution, scan rate of 50 mV s⁻¹ at 25 °C, (b) LSV recorded in 0.5 M H₂SO₄ O₂-saturated solution, 900 rpm, scan rate of 5 mV s⁻¹ at 25 °C, (c) Capacitance plot, (d) Nyquist plot, (e, f) R_Σ and C_{lim} of electrocatalysts obtained at DC bias potential of 0.425 V_{RHE}.

271

272 3.3 Electroactivity of electrocatalysts

273 **Figure 6a** shows the CVs of electrocatalysts. All electrocatalysts exhibited two anodic and two cathodic peaks with
 274 well reversibility in hydrogen region that can be assigned to uniform dispersed polycrystalline Pt particles over the
 275 surface of the supports. For all electrocatalysts, the CVs exhibit the three characteristic regions: the hydrogen
 276 ad/desorption peaks appear at a potential range between 0.06–0.36 V_{RHE}, the double layer capacitance, and the region
 277 of Pt oxide formation with the reduction in the higher potential [22,55,57–60]. The Pt/NbO/CNTs electrocatalyst
 278 exhibited earlier Pt reduction cathodic peak at 0.76 V_{RHE} compare to other catalysts, and highest ECSA value of
 279 81.62 m² g⁻¹ compare to Pt/CNTs and Pt/C with ECSA value of 76.85 and 73.66 m² g⁻¹, respectively (**Table 2**). The
 280 presence of NbO on hybrid support plays a favorable role, which attributed to uniform dispersion of Pt NPs over the
 281 NbO/CNTs hybrid support and faster polishing the Pt surface from formed oxide [14,22–25].

282 **Figure 6b** compares the ORR activity of electrocatalysts. All electrocatalysts exhibited diffusion-controlled regime
283 at a potential less than $0.6 V_{\text{RHE}}$, reaching limiting current densities between $5\text{--}5.5 \text{ mA cm}^{-2}$. The region of mixed
284 diffusion kinetic control is in potential range of $0.6\text{--}0.9 V_{\text{RHE}}$, and kinetic region is in potential higher than $0.9 V_{\text{RHE}}$.
285 The Pt/NbO/CNTs shows high ORR electroactivity with onset potential of $1.0 V_{\text{RHE}}$ for O_2 reduction as well as high
286 half-wave potential of $0.86 V_{\text{RHE}}$ compared to a halfwave potential of 0.83 and $0.81 V_{\text{RHE}}$ for Pt/CNTs and
287 commercial Pt/C, respectively. The Pt/NbO/CNTs achieved outstanding ORR activity, producing 1.14 mA cm^{-2} at
288 $0.9 V_{\text{RHE}}$ compared to only 0.86 and 0.57 mA cm^{-2} for Pt/CNTs and commercial Pt/C. In general, the ORR initiates
289 by O_2 molecular adsorption on the surface of Pt electrocatalyst. The Pt- O_2 either hydrogenated to Pt-OOH ($\text{O}_2 + \text{H}^+$
290 $+ \text{e}^- \rightarrow \text{OOH}$), which later dissociates into adsorbed O and OH, or undergoes direct splitting of the O-O bond in the
291 presence of oxygen vacancy sites on the NbO support that resulted to hydrogenation of O or OH to H_2O [14,61,62].
292 Surface defects on NbO, especially oxygen vacancies, have been considered as active sites for water splitting. In
293 fact, employing NbO support has the undoubted advantages of reducing the OH adsorption on Pt surface and
294 preventing the dissolution of Pt from the surface of the support [1,7]. Also, the enhancement in ORR activity of
295 Pt/NbO/CNTs could be correlated with reduction of the Pt d-bond length, due to the SMSI between NbO support
296 and Pt NPs that weakens the interaction between Pt and the adsorbed oxygenated species and leads to higher
297 electroactivity compared to that Pt/CNTs and commercial Pt/C catalysts [21,49,63,64]. Tafel Plots using mass-
298 transfer-corrected kinetics are shown in (inset of **Fig. 6b**). The electrocatalysts display similar trends, indicating that
299 the order of reaction should be the almost the same, while Pt/NbO/CNTs exhibited faster kinetics reaction at high
300 potential compare to Pt/CNTs and Pt/C. The Tafel plot shows double slop region, lower Tafel slope at high potentials
301 (-59.2 mV/dec) compared to that at low potentials (-118.4 mV/dec) due to site-blocking effect by OH or O at high
302 potentials cause the Tafel slope to deviate from its intrinsic value at low potentials [65,66]. Moreover, to understand
303 the influence of NbO support on electron-transfer kinetics involved in the ORR, and determine the mechanism of
304 reaction, (whether O_2 is reduced directly to water via a direct 4 electrons or an indirect two-step 2+2 electrons),
305 polarization curves of ORR were measured at various rotation speed (**Fig. S2**). Both Pt/NbO/CNTs and Pt/CNTs
306 electrocatalysts exhibited an enlarged current intensity by increasing the rotation speed, due to the enhancement of
307 O_2 diffusion to catalyst layer [49]. The Koutecky-Levich plot shows linear trend with a parallel slope at different
308 potentials for both catalysts, enabling the calculation of the number of electrons, equal to 4.18 and 3.9 for
309 Pt/NbO/CNTs and Pt/CNTs, respectively (**Fig. S2**).

310

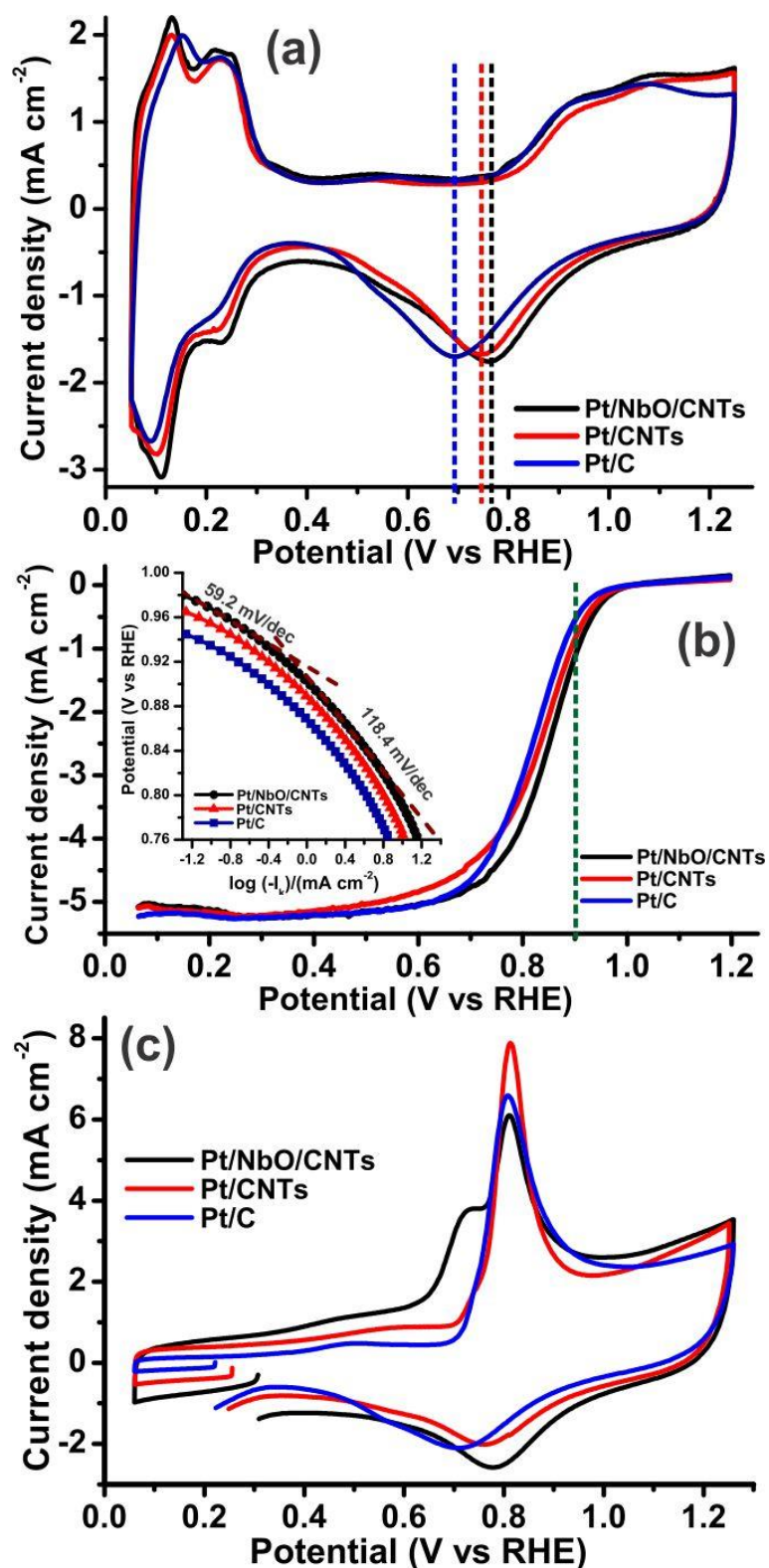
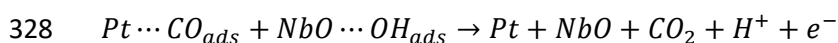
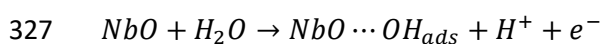


Figure 6. Electroactivity of catalysts; (a) CV recorded in 0.5 M H_2SO_4 N_2 -saturated, scan rate of 50 mV s^{-1} ; (b) LSV recorded in 0.5 M H_2SO_4 O_2 -saturated, 900 rpm, scan rate of 5 mV s^{-1} ; (c) CV of CO oxidation recorded in 0.5 M H_2SO_4 , scan rate of 20 mV s^{-1} .

311

312 **Figure 6c** shows CO stripping voltammograms obtained for electrocatalysts. The Pt/NbO/CNTs shows an
 313 enhancement in CO oxidation activity, attributed to a faster removal of CO species. The Pt/NbO/CNTs displays a

314 double shoulder peak of CO oxidation, due to NbO support and Pt crystals orientation in structure of electrocatalyst,
 315 which weakens bonding with CO [67]. The Pt/NbO/CNTs displays the earlier onset potential of 0.3 V_{RHE}
 316 corresponding to CO oxidation with an evident pre-shoulder at potential of 0.6 V_{RHE}, achieving to maximum current
 317 at 0.8 V_{RHE}. On the other hand, both Pt/CNTs and Pt/C catalysts present onset and maximum current of CO oxidation
 318 at potential of 0.71 and 0.8 V_{RHE}, respectively. In addition, The Pt/NbO/CNTs exhibited the cathodic Pt reduction
 319 peak at earlier potential of 0.79 V_{RHE}, compared to Pt/C and Pt/CNTs. Employing NbO as a support has the
 320 advantages of weakening the CO adsorption on Pt surface by lateral repulsion from the OH or O on the suboxide's
 321 support surface and stripping the CO from the Pt surface in lower potential. In fact, water dissociation over the
 322 metals oxide support starts at lower potential to provide OH species at the interface Pt-NbO, which results to
 323 reducing the anodic overpotential, while CO species are going to be oxidized to CO₂ over the Pt-NbO interface.
 324 Moreover, availability of NbO oxygen vacancy on the surface helps to oxidize the adsorbed CO on Pt surface faster,
 325 and the oxides surface is replenished through a redox reaction with water [28,68–70]. **Table 2** summarizes the key
 326 parameters of the electrocatalysts characterization;



329

Table 2. Electrochemical characterization of electrocatalysts

Catalyst	NbO [wt.%]	Pt [mg cm ⁻²]	ECSA _{H₂} * [m ² g ⁻¹]	ECSA _{CO} ** [m ² g ⁻¹]	I @ 0.9 V [mA cm ⁻²]	Mass activity [mA mg ⁻¹]
Pt/NbO/CNTs	19	0.02	81.62	88.43	1.14	57
Pt/CNTs	-	0.02	76.85	83.27	0.86	43
Pt/C	-	0.02	73.66	82.56	0.57	28.5

*The ECSA was determined by integrating the charge associated with H-UPD (210 mC cm_{Pt}⁻²)

**The ECSA was determined by integrating the charge associated with CO-UPD (420 mC cm_{Pt}⁻²)

330

331 **3.4 Durability of electrocatalysts**

332 **Protocol (I): Cycling through Pt oxide growth/removal**

333 In addition to high electrocatalytic activity, stability and durability are important factors for electrocatalysts in order
 334 to be considered for PEMFC application. The ex-situ stability test was performed on all catalysts using AST
 335 protocol, which subjects each catalyst to triangular-wave form potential cycling in the range of 0.05-1.25 V_{RHE} in
 336 0.5 M H₂SO₄ at 25 °C. Under this protocol the stability of Pt NPs against agglomeration/dissolution over the support
 337 was evaluated. We have found that this protocol exacerbates Pt NPs size growth since it cycles through Pt oxide
 338 growth/stripping without causing corrosion on most carbon supports [46,48,56]. **Figure 7a** shows the AST results
 339 on Pt/NbO/CNTs electrocatalyst for 5000 potential cycles performed with scan rate 100 mV s⁻¹. The Pt/NbO/CNTs
 340 catalyst shows an interesting stability and durability performance compare to Pt/CNTs and Pt/C catalysts (**Fig. 7a,**
 341 **7b and S2**). The Pt/NbO/CNTs shows virtually no changes over the course of stability with only 5% loss of its
 342 ECSA, while Pt/CNTs and Pt/C presented 64.4% and 73.2% loss of ECSA, respectively (**Fig 7c**). To further
 343 investigate on stability of electrocatalysts, the EIS tests were performed, since it can provide information about
 344 changes in conductivity and resistance in the catalyst layer under different conditions, as well as insight into
 345 degradation mechanisms [71–73]. **Figure 7d-7e** show the R_z and C_{dl} variation of electrocatalysts over the course of

346 stability. The Pt/NbO/CNTs shows short Warburg length assign to high electronic conductivity of NbO/CNTs
 347 support and R_{Σ} follow stable trend during stability means no change in ionic and electronic conductivity of support.
 348 Both Pt/CNTs and Pt/C catalysts show decreasing in R_{Σ} during AST due to enhanced catalyst layer hydration. The
 349 Pt/NbO/CNTs exhibited almost no change in C_{dl} owing to excellent stability of the catalyst surface layer and Pt NPs,
 350 while Pt/CNTs and Pt/C exhibited decreasing in C_{dl} , characteristic response of Pt NPs agglomeration/dissolution in
 351 absence of support corrosion [74,75]. The ORR activity of catalysts was assessed before and after the AST (**Fig.**
 352 **7f**). The Pt/NbO/CNTs exhibits outstanding activity, with a high onset potential of $1V_{RHE}$ for O_2 reduction followed
 353 by high half-wave potential ($E_{1/2}$) of $0.86 V_{RHE}$ compared to a half-wave potential of 0.83 and $0.81 V_{RHE}$ for the
 354 Pt/CNTs and commercial Pt/C (**Fig. S3**). Pt/NbO/CNTs illustrated excellent durability by only loss 12.6% of its
 355 initial mass activity at $0.9 V_{RHE}$ by shifting to lower potential, while Pt/CNTs and Pt/C exhibited massive
 356 degradation, losing 52% and 75% of their initial ORR activity at $0.9 V_{RHE}$ respectively. (CV, EIS and ORR plots for
 357 this AST can be found in **Fig. S3**).

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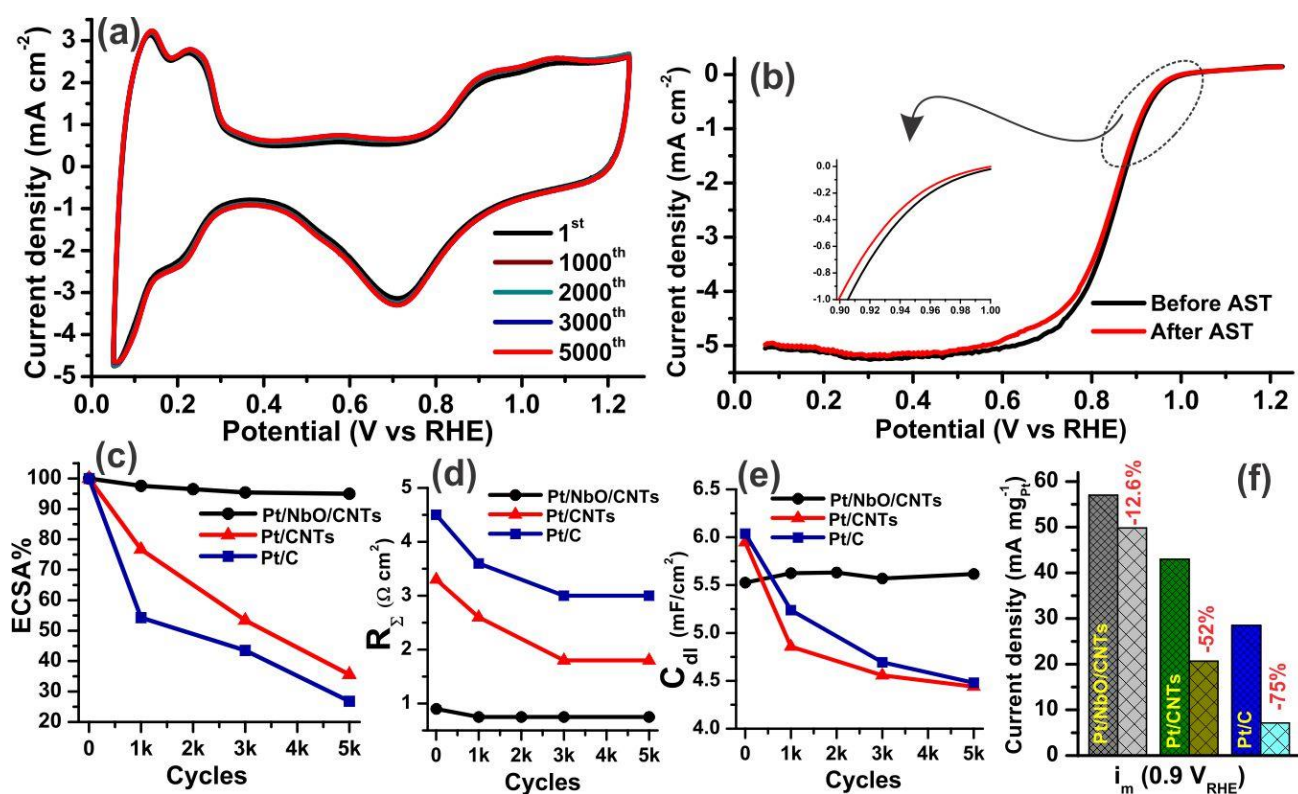


Figure 7. (a) Variation in the CV response of the Pt/NbO/CNTs, (b) ORR activity of Pt/NbO/CNTs before and after AST, (c) ECSA variation of the electrocatalysts over the course of AST (protocol I), (d, e) R_{Σ} and C_{lim} of electrocatalysts obtained at DC bias potential of $0.425 V_{RHE}$, (f) ORR mass activity (i_m) of electrocatalysts.

359

360 Protocol (II): Ex-situ Load Cycling

361 The ex-situ stability of electrocatalysts were evaluated according to fuel cell load cycling via triangular-wave
 362 potential cycling in the range of $0.6-1 V_{RHE}$ for 30,000 cycles in $0.5 M H_2SO_4$ at $25 ^\circ C$. This US Department of
 363 Energy (DoE) based protocol is commonly used to evaluate the stability of Pt NPs against dissolution/agglomeration
 364 [76–79]. In fact, this stability test shows the significance of SMSI effect on stabilization of Pt NPs over the

365 supporting materials under fuel cell relevant conditions that avoids support corrosion. The change in key
 366 electrochemical parameters over the course of this AST for each catalyst is shown in **Figure 8**. Pt/NbO/CNTs
 367 exhibited excellent stability by showing only a 7.4% decay in ECSA, with no change in CV shape. This indicates a
 368 strong interaction between Pt NPs and NbO/CNTs support (**Fig. S3**). The Pt/CNTs and commercial Pt/C show 18.3%
 369 and 47.6% decay in ECSA, which indicated Pt NPs are more stable on CNTs support [80,81]. The EIS responses
 370 for all catalysts showed that the R_{Σ} decreased over the initial 5000 cycles of AST due to enhanced catalyst layer
 371 hydration (**Fig. 8b**). On the other hand, C_{dl} of both Pt/NbO/CNTs and Pt/CNTs catalysts after slight increase at
 372 beginning, remained almost unchanged over the course of AST (**Fig. 8c**), while the Pt/C illustrated 12% decrease
 373 on C_{dl} over the course of AST, which is characteristic of Pt NPs dissolution/agglomeration being the dominant
 374 degradation mechanism of catalyst [73]. The ORR activity of all catalysts was assessed before and after the AST
 375 (**Fig. 8d**). The Pt/NbO/CNTs and Pt/CNTs electrocatalysts showed ORR activity (i_m) decline of 7%, and 23.4% of
 376 their initial after 30K cycling under AST, respectively, while Pt/C loss 41.2% of its ORR activity. The Pt/NbO/CNTs
 377 exhibited only 5.5 mV decrease in $E_{1/2}$, while 15 and 40 mV decay in $E_{1/2}$ was observed for Pt/CNTs and Pt/C
 378 electrocatalysts, respectively. According to US DoE targets, electrocatalysts should not loss more than 40% of their
 379 initial activity after stability testing under load cycling protocol (0.6-1 V_{RHE}), which in this regard both
 380 Pt/NbO/CNTs and Pt/CNTs could meet the DoE target. (CV, EIS and ORR plots for this test can be found in **Fig.**
 381 **S4**).

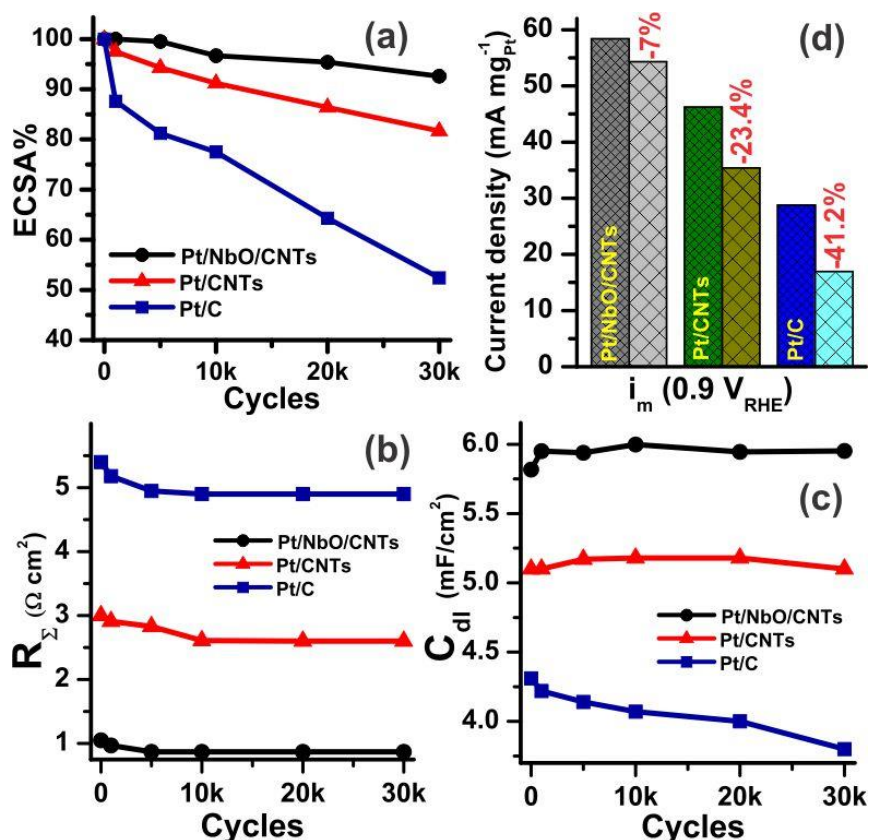


Figure 8. (a) ECSA variation of the electrocatalysts over the course of AST (protocol II), (b, c) R_{Σ} and C_{lim} of electrocatalysts obtained at DC bias potential of 0.425 V_{RHE} , (d) ORR mass activity (i_m) of electrocatalysts.

382

383

384 **Protocol (III): Ex-situ Startup/Shutdown**

385 The *ex-situ* stability of electrocatalysts was evaluated according to fuel cell vehicle startup-shutdown condition,
386 using a potential triangular-wave form between 1-1.5 V_{RHE} at a scan rate of 500 mV/s in 0.1 M H_2SO_4 for 10,000
387 cycles. By employing this protocol, the stability of NbO/CNTs, and carbon supports against corrosion and stability
388 of Pt NPs over the supports against dissolution/agglomeration were assessed [82]. Over the course of stability test
389 no sign of degradation was observe on double layer region of Pt/NbO/CNTs catalyst. The ECSA was remained quite
390 stable, showing only 11.4% decay comparable with Pt/CNTs and Pt/C, which loss 32.2% and 78.5% of their initial
391 ECSA, respectively (**Fig. 9a**). The EIS response of Pt/NbO/CNTs was virtually unchanged, with constant trend of
392 R_{Σ} and C_{dl} throughout the AST (**Fig. 9b-9c**). on the other hands, for both Pt/CNTs and Pt/C, the R_{Σ} increased steadily
393 throughout the AST and C_{dl} initially increased during initial 3000 cycles, due to the oxidative formation of pseudo-
394 capacitive groups on the carbon surface [77]. C_{dl} declined upon continued cycling for both electrocatalyst but more
395 intensely for Pt/C. This EIS response on C_{dl} (initially increasing and then decreasing) follow by increasing in R_{Σ} , is
396 characteristic of carbon support corrosion [73]. **Figure 9d** compares the ORR activity (i_m) of all catalysts before and
397 after the AST. Pt/NbO/CNTs showed high durability by only a 7 mV and 17.1% decay in $E_{1/2}$ and ORR mass activity
398 after 10,000 cycles, respectively. On the other hand, Pt/CNTs and Pt/C show 24 mV and 106 mV decay in $E_{1/2}$,
399 respectively, follow by loss of 40.45% and 93% of their initial activity, due to Pt NPs sintering and carbon corrosion.
400 According to DoE statement, electrocatalysts shouldn't loss more than 40% of their initial activity under startup-
401 shutdown (1 - 1.5 V_{RHE}) stability test. In this regard, Pt/NbO/CNTs showed high stability and durability, which
402 makes it suitable electrocatalyst for ORR. (CV, EIS and ORR plots for this AST can be found in **Fig. S5**). Also
403 listed in **Table 3** are the reported electroactivity and stability of several other catalysts that employ metal oxide-
404 based supports.

405

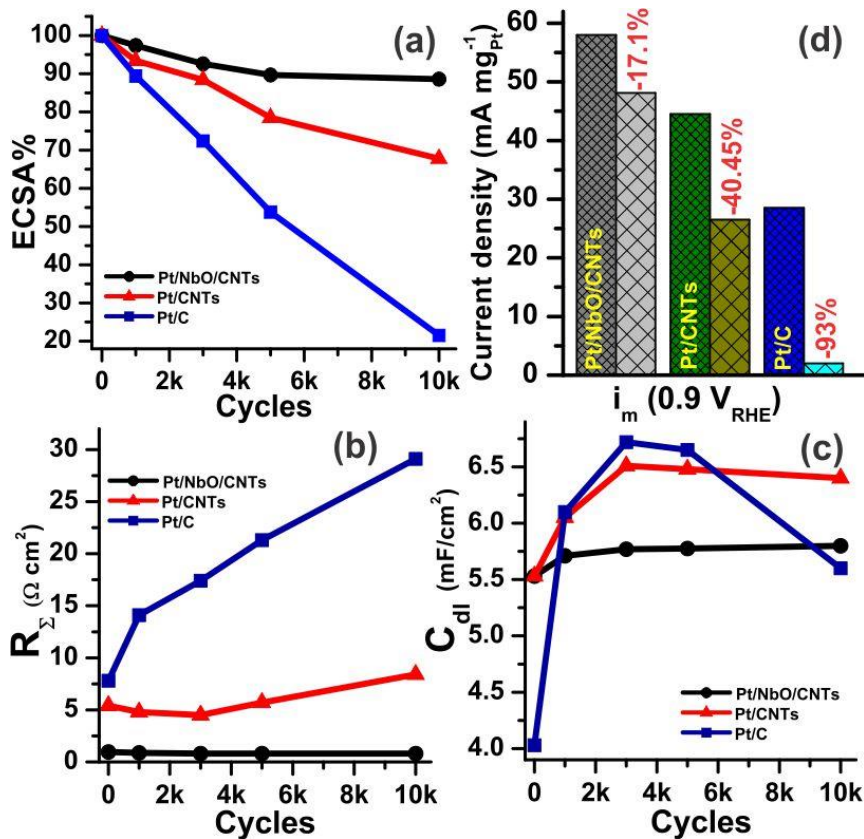


Figure 9. (a) ECSA variation of the electrocatalysts over the course of AST (protocol III), (b, c) R_{Σ} and C_{dl} of electrocatalysts obtained at DC bias potential of 0.425 V_{RHE}, (d) ORR mass activity (i_m) of electrocatalysts.

406

Table 3. Electrochemical characterization of electrocatalysts

Catalyst	Pt mg cm^{-2}	ECSA $\text{m}^2 \text{g}^{-1}$	I @ 0.9 mA/mg_{Pt}	I @ 0.9 mA cm^{-2}	Media	Stability protocol	ECSA loss cycle	Ref.
Pt/NbO/CNTs	0.02	81.62	57	1.14	0.5M H ₂ SO ₄	(I)	5%-5k	current study
						(II)	7.4%-30k	
						(III)	11.4%-10k	
Pt/CNTs	0.02	76.85	43	0.86	0.5M H ₂ SO ₄	(I)	64.4%-5k	current study
						(II)	18.3%-30k	
						(III)	32.2%-10k	
Pt/C	0.02	73.66	28.5	0.57	0.5M H ₂ SO ₄	(I)	73.2%-5k	current study
						(II)	47.6%-30k	
						(III)	78.5%-10k	
Pt-Ta ₂ O ₅ /CNT	0.02	78.4	-	0.29	0.1M HClO ₄	(II)	4.1%-10k	[79]
Pt/CNT	0.02	67.1	-	0.15	0.1M HClO ₄	(II)	42%-10k	[79]
Pt/C	0.02	61.9	-	0.11	0.1M HClO ₄	(II)	49.9%-10k	[79]
Pt/TiO ₂ /G-ATV	0.101	40.4	4.95	0.5	0.5M H ₂ SO ₄	(I)	77%-4k	[4]
Pt/TiO ₂ -CN _x	-	75	<10	-	0.5M H ₂ SO ₄	(II)	3%-1k	[83]
Pt/NbO ₂ /C	0.005	68	-	1	0.1M HClO ₄	(II)	45%-30k	[1]
Pt/PdCu/C	0.02	83.2	-	2.5	0.1M HClO ₄	(I)	30%-0.5k	[84]
Pt/IrO ₂ Nb ₂ O ₅ -rGO	0.057	69.5	8.5	0.48	0.5M H ₂ SO ₄	(I)	23.8%-2k	[85]
Pt/TiO _x /CNT	0.0136	44.13	10.7	0.3	0.1M HClO ₄	(I)	<1%-4k	[7]

407

408

409

410 **3.5 Performance of Pt/NbO/CNTs on PEMFC**

411 **Figure 10a** shows the polarization and power density curves achieved using the Pt/NbO/CNTs electrocatalyst at the
412 cathode, running the PEMFC at different temperatures. The performance at 80 °C was compared to that of a MEA
413 with Pt/C electrodes at both sides (**Fig. 10b**); the Pt/NbO/CNTs reached a maximum of power density of 772 mW
414 cm⁻², respect to 680 mW cm⁻² of the Pt/C. These results indicate an enhanced electroactivity of Pt supported on
415 hybrid NbO/CNTs support towards ORR. The high power density of Pt/NbO/CNTs can be attributed to the good
416 charge transfer between Pt and NbO support, which favors the oxygen reduction kinetics [17,86]. In fact, supporting
417 materials can have a great influence on the activity of electrocatalysts by promoting the diffusion of reactants and
418 products [9,35,87,88].

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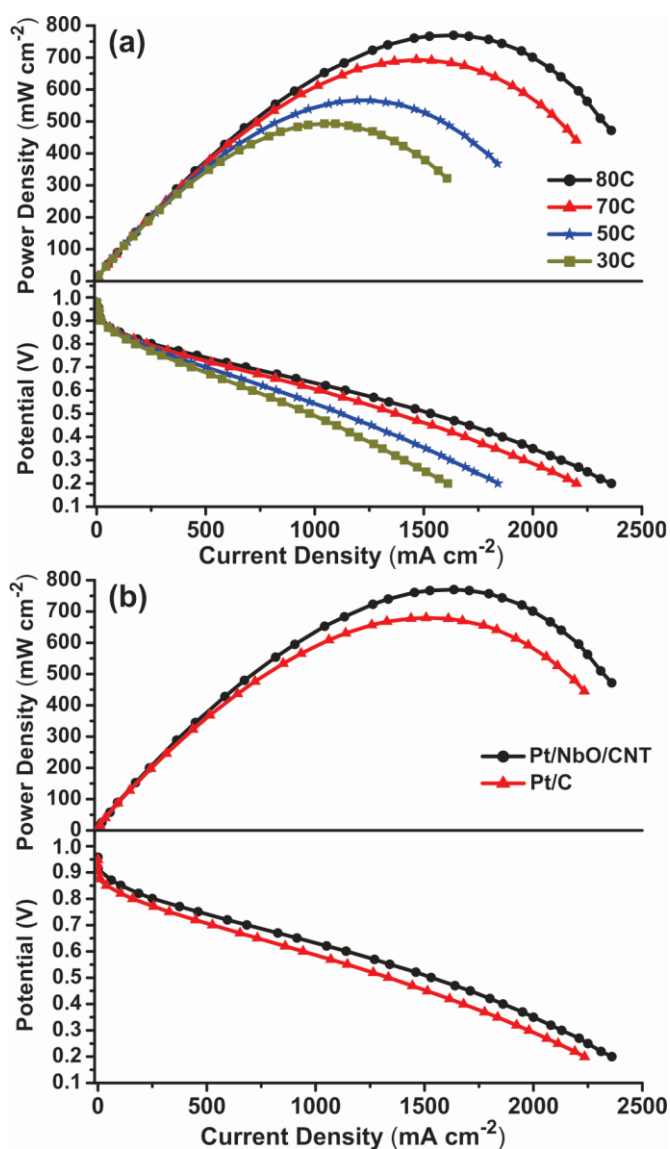


Figure 10. (a) PEMFC performance of the Pt/NbO/CNTs, polarization and power density curves as a function of the temperature, (b) Comparison of the fuel cell performance obtained using the Pt/NbO/CNTs and Pt/C electrodes. Measurements were made in a 5 cm² single cell PEMFC at 80 °C, using a Pt loading of 0.15 mg cm⁻². H₂ flow rate of 120 nml min⁻¹ 100% RH 1 bar bp; O₂ flow rate 200 nml min⁻¹ 100% RH 1 bar bp, and membrane of NRE212.

420 The short-term stability on the Pt/NbO/CNTs electrode was assessed by maintained in operation at the maximum
 421 current density at 80 °C for 96 consecutive hours and Polarization curves were collected every 24 hours. **Figure 11**
 422 demonstrate the excellent stability of Pt/NbO/CNTs electrode, which lost only 4% of its maximum power, from 770
 423 to 740 mW cm⁻², confirming the high stability of Pt/NbO/CNTs catalyst as already demonstrated with AST under
 424 both load cycling and Startup/Shutdown. Considering the DoE guidelines of target MEAs able to reach the
 425 equivalent of 5 mW μg_{Pt}⁻¹ as mass specific power density (or a Pt usage equivalent to 200 mg_{Pt} kW⁻¹) [89,90], with
 426 the mass of Pt accounting for both anode and cathode loading, the Pt/NbO/CNTs electrode achieved a mass specific
 427 power density of almost 2.6 mW μg_{Pt}⁻¹ (390 mg_{Pt} kW⁻¹). Considering also the high stability demonstrated in almost
 428 100 hours of continuous operation, the Pt/NbO/CNTs catalyst can be considered as a promising low-Pt catalyst
 429 alternative to Pt/C for PEMFCs.

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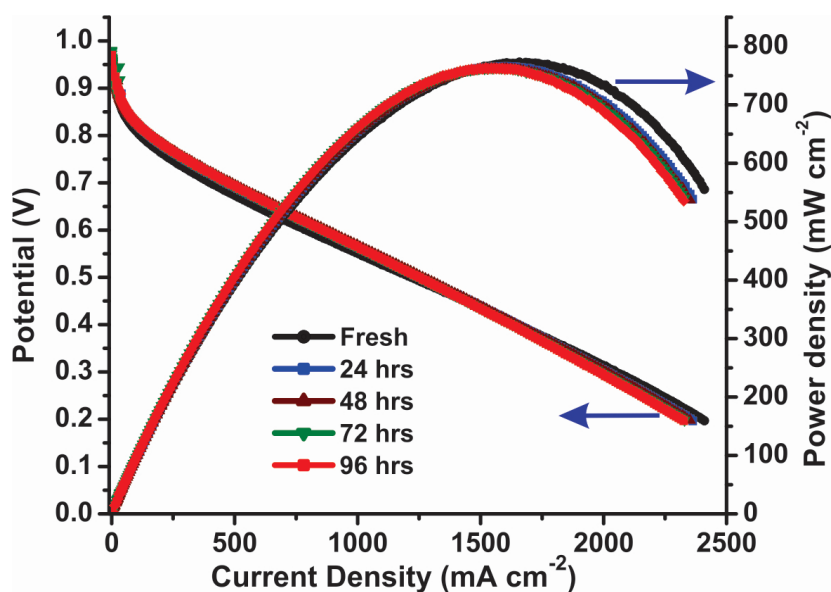


Figure 11. *in-situ* Short-term stability of Pt/NbO/CNTs. Measurements were made in a 5 cm² single cell PEMFC at 80 °C using a Pt loading of 0.15 mg cm⁻². H₂ flow rate of 120 nml min⁻¹ 100% RH 1 bar bp; O₂ flow rate 200 nml min⁻¹ 100% RH 1 bar bp, and membrane of NRE212.

431

432 Conclusions

433 This study demonstrated the NbO as an excellent metal oxide support, in combination with multi-walled carbon
 434 nanotubes (CNTs), to enhance the electrocatalytic activity of Pt towards the oxygen reduction reaction. The highly
 435 electroactive and stable electrocatalyst, synthesized by depositing Pt over a NbO/CNTs hybrid support, was used to
 436 fabricate low Pt loading MEA for PEMFC. The developed Pt/NbO/CNTs electrocatalyst showed high ORR activity
 437 comparable to Pt/CNTs and commercial Pt/C. Also, the Pt/NbO/CNTs exhibited excellent stability under both load
 438 cycling and Startup/Shutdown AST protocols. The Pt/NbO/CNTs electrode achieved to maximum power density of
 439 770 mW cm⁻² under fuel cell application, with only negligible decline in electroactivity (loss of power of only 4%
 440 after 96 consecutive hours of operation at 80 °C). The NbO support, in combination with CNTs, may not only
 441 improve corrosion resistance of carbon support, also promote catalytic activity and durability of Pt electrocatalyst
 442 through strong metal-support interactions. NbO demonstrated as a promising support for Pt electrocatalyst, with the

443 ability to mitigate one of the major problems involving carbon corrosion in acidic media. Moreover, the good
444 performance on PEMFC obtained with a low Pt loading on the MEA makes the Pt/NbO/CNTs an excellent electro-
445 active and stable catalyst to boosting applications of PEMFC on the market.

446

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452

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